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Electrolytic Treatment of Oily Wastewater from Manufacturing and Machining Plants

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A pilot plant unit capable of processing about 5700 l/day (1500 gal/day) was designed, constructed, and evaluated at an actual plant site. Operating parameters and process equipment were evaluated to assess the potential and problems of the process.

Wastewater with initial oil concentrations in the range of 300 to 7,000 ppm of solvent extractables has been reduced to less than 50 ppm in 90% of the test runs, and to less than 25 ppm in 83%. These test runs were done at conditions of minimum operating cost and minimum sludge generation. When necessary, Freon extractables generally are reducible to about 10 ppm or less by the addition of more electrolytically dissolved iron to the system at a small increase in cost.

Preliminary economics look favorable and overall results are quite encouraging so that further scale-up of the process is recommended.

This report was submitted in fulfillment of Grant No. S-804174 by Ford Motor Company under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period May 18, 1976 to August 17, 1978, and work was completed as of August 17, 1978.

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June 1980

ELECTROLYTIC TREATMENT OF OILY WASTEWATER FROM MANUFACTURING AND MACHINING PLANTS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes a continuous electrolytic treatment process for removal of emulsified oil from dilute oily wastewater streams, such as is generated in metal working operations. Results obtained from operating a pilot plant facility demonstrate the feasibility of the process. The electrolytic process may offer an alternative to conventional chemical treatment for small to medium size machine shops. The Industrial Pollution Control Division is to be contacted for further information.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

A continuous electrolytic treatment is being developed to remove emulsified oil from dilute oily wastewater streams, such as is generated in metal working operations. In this process, the wastewater permeates through an iron chip bed anode and steel mesh cathode. A potential is applied to the electrodes, forming ferrous ions at the anode and hydroxyl ions at the cathode. The ferrous ions react in a complex manner with the emulsifying agents, destabilizing the emulsion and generating an oil rich floating sludge and essentially oil-free water.

A pilot plant unit capable of processing about 5700 l/day (1500 gal/day) was designed, constructed, and evaluated at an actual plant site. Operating parameters and process equipment were evaluated to assess the potential and problems of the process.

Wastewater with initial oil concentrations in the range of 300 to 7,000 ppm of solvent extractables has been reduced to less than 50 ppm in 90% of the test runs, and to less than 25 ppm in 83%. These test runs were done at conditions of minimum operating cost and minimum sludge generation. When necessary, Freon extractables generally are reducible to about 10 ppm or less by the addition of more electrolytically dissolved iron to the system at a small increase in cost.

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SECTION 1

INTRODUCTION

Process wastewater from metal working operations contains free or suspended oil and emulsified oil which must be removed before the water can be discharged or reused. These oils originate mainly from parts washer overflow and machining coolant dumping, and the concentration typically ranges from 1,000 - 10,000 ppm as emulsified oil and perhaps 30,000 ppm as free suspended and floating oil. The free oil can be removed by gravity separation and a simple skimming operation, but the removal of the emulsified oil is more complicated. These oil-in-water emulsions are intimate two-phase mixtures of oil and water with oil dispersed as microscopic droplets (0.1-100 μm diameter) in the aqueous phase and stabilized by the presence of surface active compounds.

Wastewaters containing these emulsions generally are treated for discharge by pH adjustments and the addition of salts of such metals as iron or aluminum, to produce a flocculant precipitate. A common technique is to begin by treating the oily wastewater with sulfuric acid to effect a primary emulsion break. The freed oil is collected and the water phase, which still may contain up to 400 ppm of emulsified oil, is further treated with ferric chloride and sodium hydroxide. The ferric ion destabilizes the emulsion by neutralizing the charge on the emulsion droplets and precipitates as ferric hydroxide -- the oil is sorbed on and into the flocculant precipitate. These conventional methods, while yielding water of good quality, generally increase the dissolved solids content of the water and generate a voluminous sludge containing about 95% water. For small-to-medium size machining plants to install a new waste treatment facility based on chemical treatment, space limitations would present the greatest problem. The electrolytic process being developed by Ford Motor Company has the potential to overcome the limitations noted above in that it is a continuous process which requires less space, generates less dissolved solids, and produces less sludge with lower water content.

Earlier development work on this process is described in References 1-3. The method is one in which the reactive cation, iron is introduced electrolytically as a ferrous ion followed by in situ oxidation to the ferric state and subsequent precipitation as ferric hydroxide. In this method the oil-in-water emulsion is destabilized during the oxidation reaction before extensive coagulation and flocculation occur. The demulsification is thought to take place by attack on the emulsifiers by hydroxyl radicals generated during ferrous ion oxidation, as well as by direct reaction of the emulsifiers with ferrous ion. The demulsified oil is then removed by adsorption on the highly dispersed ferric hydroxide microfloc.

The objective of the present work was to develop and demonstrate on a pilot scale the electrolytic method of removing emulsified oil from oily wastewater generated by

metal fabrication operations, and to establish its technical and economic feasibility. The pilot unit was installed at the Ford Motor Company Livonia Transmission Plant and actual plant discharge was fed to the unit for treatment.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results of the electrolytic pilot unit study for treatment of oily wastewater indicate that the process is capable of rendering the wastewater suitable for direct discharge to municipal sewers and possibly to surface waters. The exact nature of the influent, however, will strongly influence the final effluent quality from the process. In these studies it was found that by operating the unit at minimum cost and minimum sludge formation to just break the emulsion, the effluent contained less than 50 ppm 90% of the time and less than 25 ppm 83% of the time, where the influent oil concentrations ranged from 300 to 7,000 ppm. Reduction in the effluent oil concentration to about 10 ppm or less generally can be accomplished, when necessary, by an increase in the iron concentration, since it was observed that the ratio of iron dissolved to oil concentration is the major parameter determining the water quality--iron concentration is controlled by controlling the current in the electrolytic dissolution of iron.

Of the other parameters examined, the salt type (added to increase ionic conductivity and prevent electrode passivation) is the next important. Calcium chloride was found to aid in the demulsification of the oily wastewater and was ordinarily the preferred salt. A concentration of 0.01N was employed in most runs. The use of calcium chloride does cause an inconvenience since calcium carbonate deposits may tend to build-up on the cathode. The pH of the as-received wastewater ranged from 8.5 to 10.5 which is typical for machining coolants. Treatment effectiveness is the same in this pH range as it is with the pH adjusted to 6.5 to 7, thus pH adjustment is unnecessary. Flow rate through the process should be fixed to handle the plant flow and slight variations in the flow do not appreciably influence the effluent.

A preliminary economic analysis indicates that the direct costs of the process (power, calcium chloride, and iron valued as scrap) can range from about $0.09 to $0.17/1000 l ($0.34 to $0.64/1000 gal) depending on the type of equipment employed in the process. Unanswered questions remain with respect to extended durability of the process, practicability of a completely automated-continuous process and the best technique for recovering oil from the generated sludge.

To answer these questions, it is recommended that the process be scaled up to approximately two to five times the pilot unit capacity and that the system be automated to achieve unattended continuous operation.

SECTION 3

EXPERIMENTAL

EXPERIMENTAL FACILITY

A schematic diagram of the electrolytic cell is shown in Figure 1. Wastewater enters the cell and permeates through a rectangular caged bed of iron or steel machining chips which acts as anode, and then through a perforated sheet metal cathode. Sufficient voltage is applied to dissolve the iron forming ferrous ions which react with the emulsifying agent freeing the oil. This oil is sorbed onto the ferric hydroxide floc which is formed in-situ by oxidation of the ferrous ion. The oil-rich ferric hydroxide sludge floats to the surface where it can be skimmed, yielding essentially oil-free water.

The electrolytic cell is constructed of 1.27 cm thick plexiglas in an angle iron frame. The cell is 91 cm wide, 61 cm high, and 244 cm long. Wastewater enters the cell through a manifold with multiple outlets to assure uniform distribution of flow through the electrode. The 7.6 cm thick anode cage is constructed of expanded titanium with diamond shaped holes with approximate size of 1.5 x 0.5 cm. Since bare titanium was found to corrode under some circumstances because of galvanic action, it was coated with a protective coating of insulating varnish which alleviated the problem.

The front face of the anodic cage is lined with a polyethylene screen with a hole size of about 0.15 cm. The screen is installed to ensure that the iron chips do not extend outward and contact the cathode or, when small enough, fall in the space between the electrodes.

The anodic cage is filled with low carbon steel chips obtained from machining operations in the plant. The optimum size of the chips was found to be 1-2 cm long and with diameter of 0.2-0.5 cm. Smaller diameter chips tend to fall through the screen, and longer ones tend to form entanglements causing difficulties in packing the chips in the anodic cage. The cathode, spaced 1.27 cm from the anode, is constructed of a perforated steel plate. A clearance of about 4 cm is maintained between the bottom of the cathode and the bottom of the anodic cage to reduce the possibility of electrical short circuiting by loose iron chips. The cathode height was extended up to about 1 cm below the water level to allow oily sludge to float over it and avoid sludge accumulation between the electrodes. Demulsification reactions and sludge flotation occur in the remaining length of the cell.

The introduction of air for oxidation of the ferrous ion and for flotation of the sludge is accomplished by forcing air through a porous membrance on the cell bottom. The membrane has an average pore size of 1 μm. In later experiments, the use of dissolved air flotation in place of air bubble flotation was evaluated.

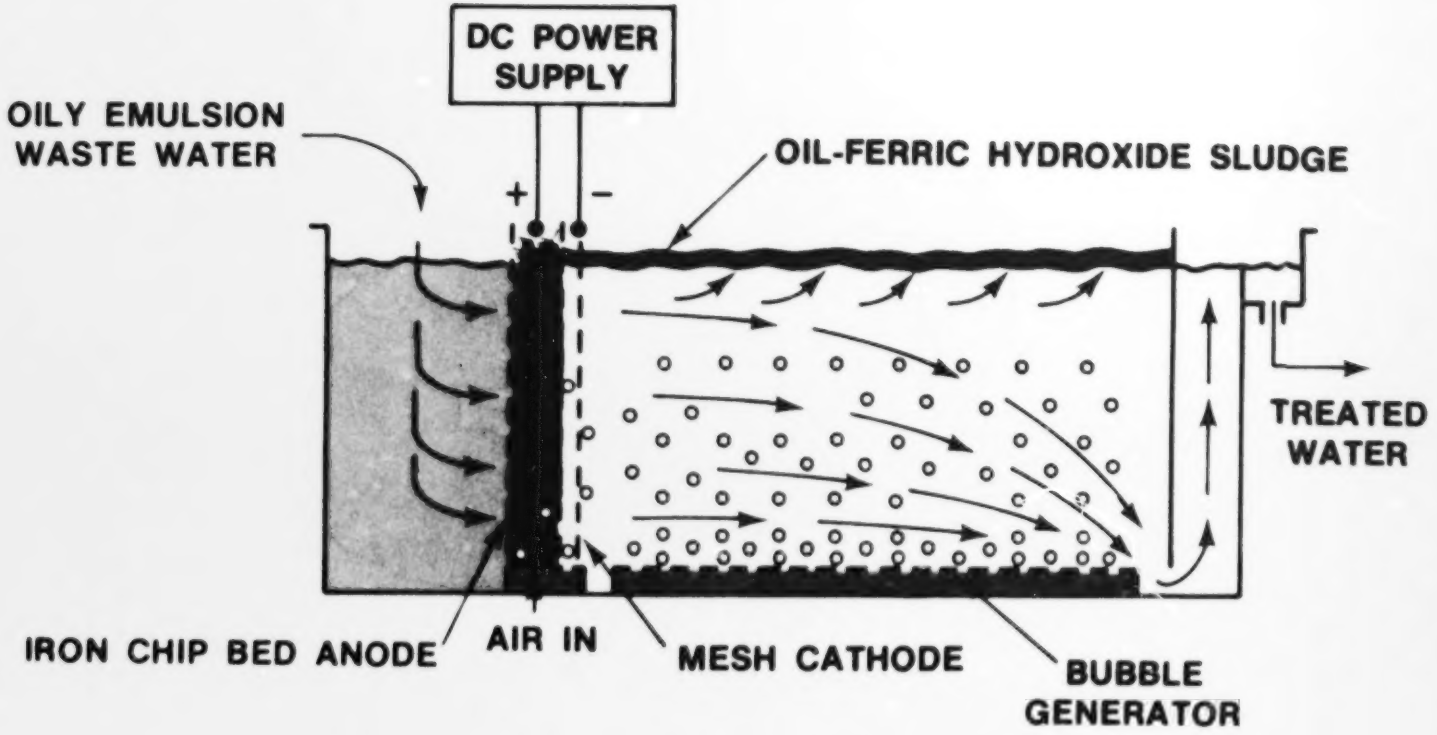

Figure 1. A schematic diagram of the electrolytic cell

The cell and ancillary equipment (pumps, sand filter, sludge skimmer, power supplies, etc) are installed in a specially constructed enclosure within the plant. A flow diagram for the system is shown in Figure 2, and photographs of the cell and system are shown in Figures 3 through 6. The 11.3 m^3 (3000 gal) wastewater receiving and storage tank is outside the enclosure but inside the plant. Nominal capacity of the system is about 3.8 l/min (1 gal/min).

EXPERIMENTAL PROCEDURE

Both simulated and actual plant wastewater were processed through the cell. The simulated wastewater was processed according to techniques developed in the laboratory to evaluate the overall cell performance and to compare the operational parameters to those obtained in previous experiments with a laboratory bench size unit.

Simulated wastewater was prepared by continuous flow mixing of machining coolant emulsion concentrate with water in a ratio to give the desired oil concentration. The standard evaluations were carried out using 2,000 ppm emulsified oil processed at 3.8 l/min (1 gal/min) using a current of 25 amp with an average potential of 15 v for 8 hr. Hydrochloric acid was added to adjust the pH to 7 and sodium chloride was added to maintain the conductivity at 1500 μmho/cm (0.58 g/l of sodium chloride). Results of these experiments indicated that steady-state conditions are reached after about 6 hr of operation which is approximately 1.5 times the plug flow residence time. This is seen in Table 1 which shows turbidity reading in nephelometer turbidity units (NTU) as a function of time and position in the cell past the cathode.

Before October 1977, the plant wastewater, which was collected from the combined plant wastewater wet well over a period of 2 hours, was carried in mobile tanks to the receiving tank in batches of about 11.3 m^3 (3000 gal). Prior to processing, the plant effluent was analyzed for pH, conductivity, turbidity, dissolved and suspended solids, and Freon extractables. Several runs were made with each of the batches in which the current and/or the flow rates were varied and the corresponding effluent quality determined. Each run lasted 6-8 hours and used about 1.89 m^3 (500 gal) of wastewater. Before passing through the cell, sodium chloride or calcium chloride may be added for conductivity and to avoid anode passivation, (which would result in current being expended to generate oxygen rather than dissolve iron), and the pH may be adjusted with hydrochloric acid. Following the electrolytic treatment the water may be passed through a sand filter to remove suspended solids. Some batches, when received, were treated with about 7.6 l of household bleach and 200 g of cupric chloride to minimize bacteria growth and odor development because of long standing in the receiving rank. Laboratory batch experiments indicated that the bleach and cupric chloride addition did not significantly influence the emulsion stability.

In October 1977 a pumping system which can continuously supply the pilot unit with fresh wastewater was installed. The inlet of the pumping system is located at a manhole which receives wastewater from most of the plant operations via three streams. The composition of wastewater delivered to the pilot unit was found to be essentially the same as that received at the wet well of the wastewater treatment plant.

After the installation of the pumping system the receiving tank could be filled daily with enough water for one day of operation. Because it was now convenient to

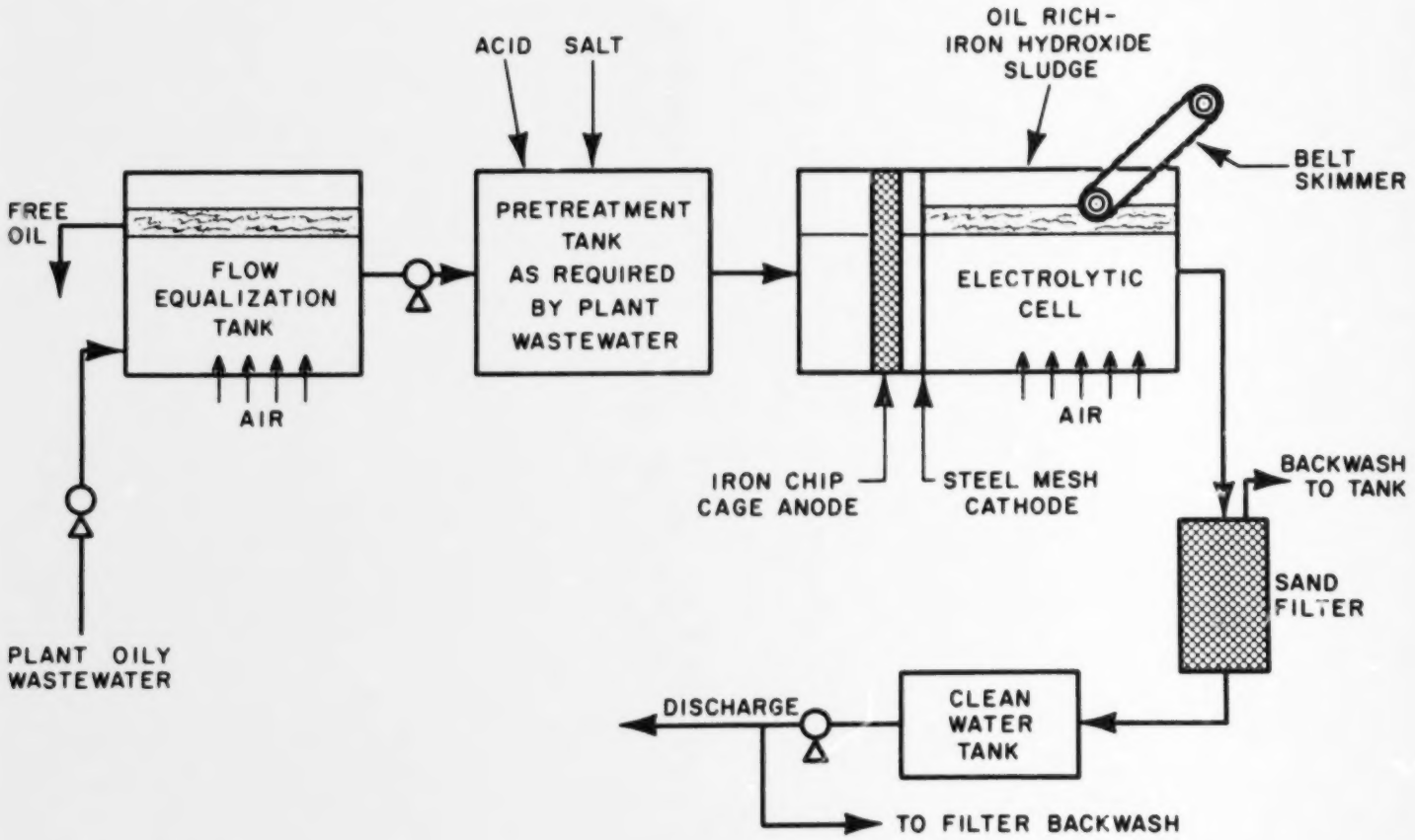

Figure 2. A flow diagram of the electrolytic process

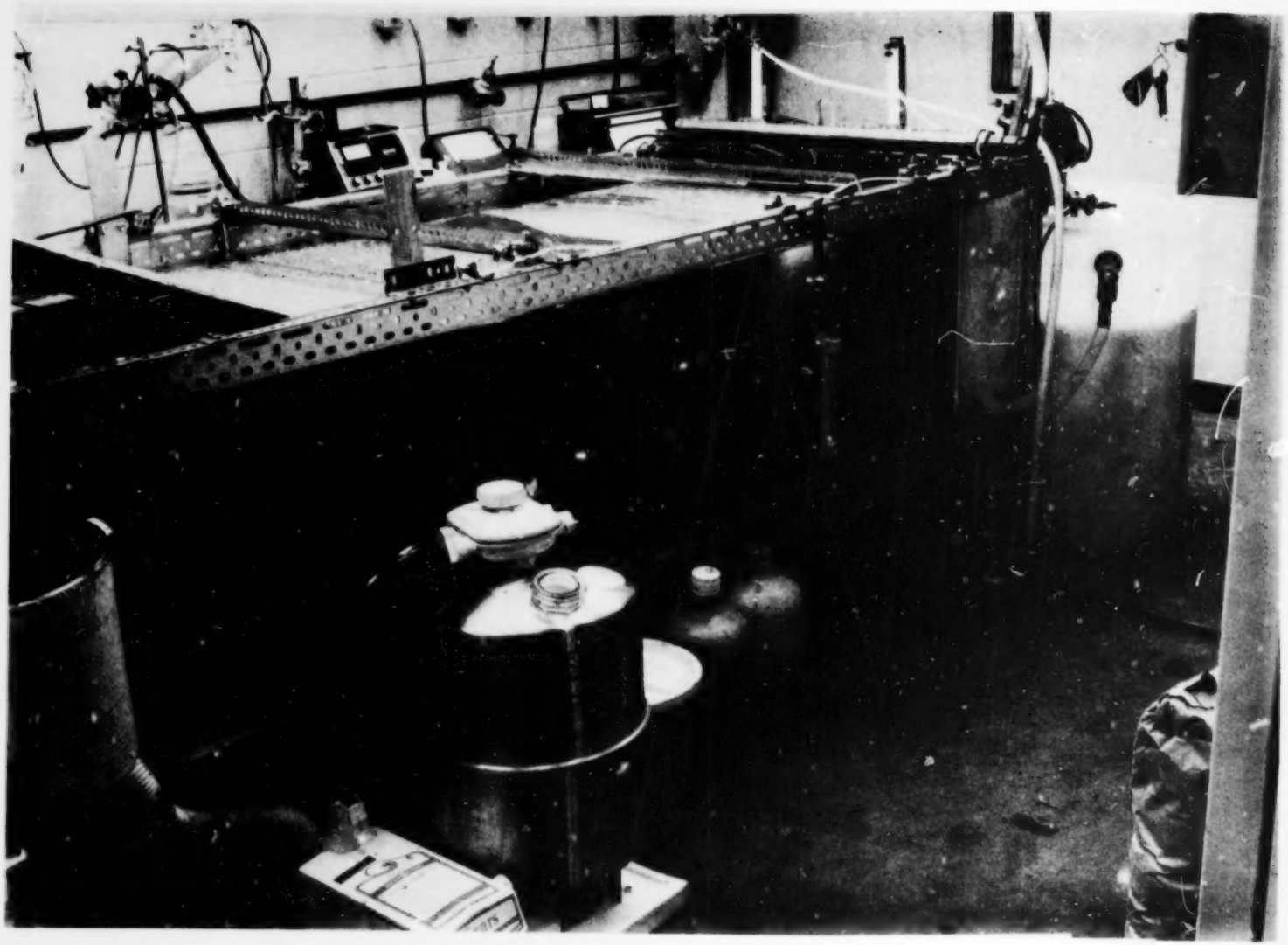

Figure 3. Experimental electrolytic treatment test facility

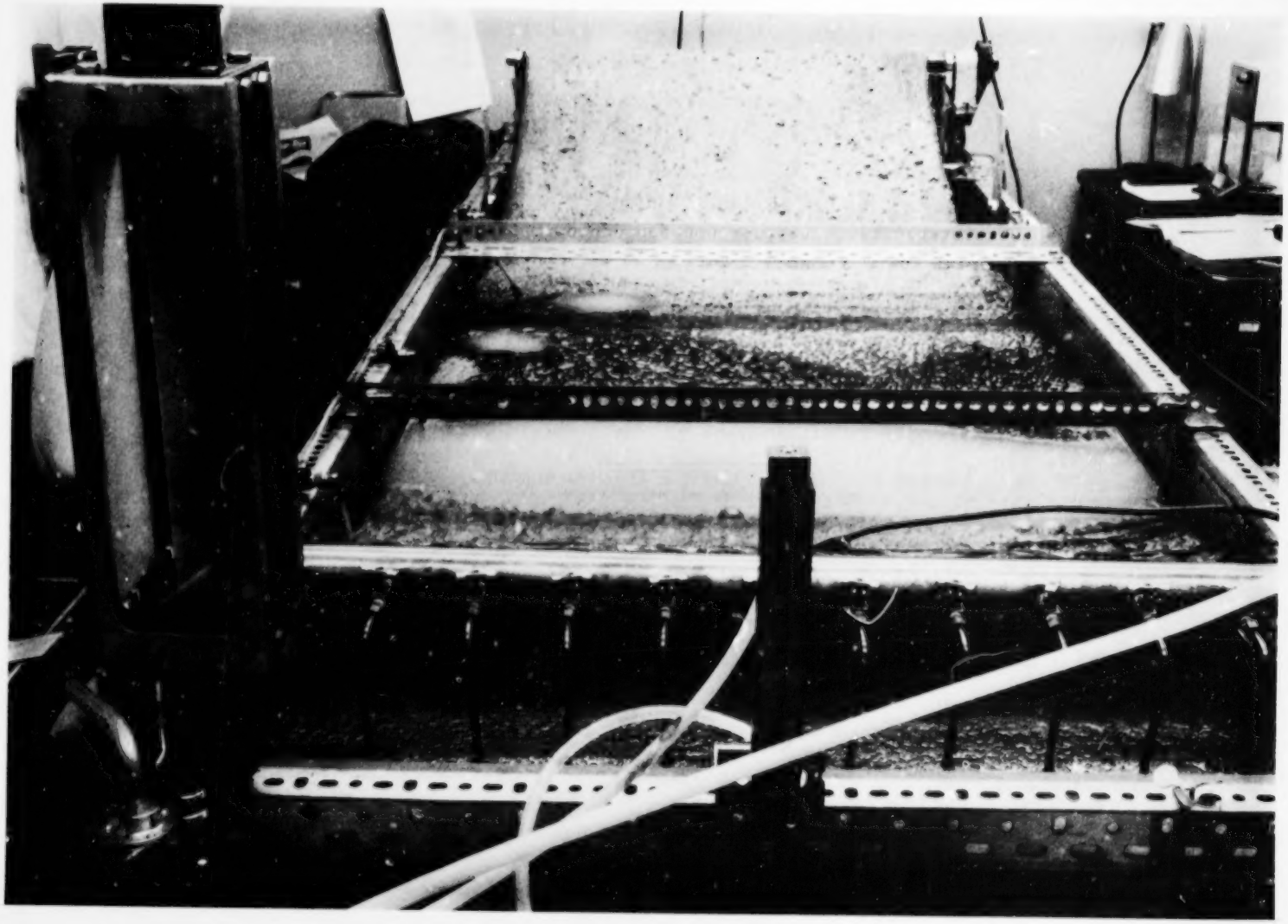

Figure 4. Flow cell, view from upstream end

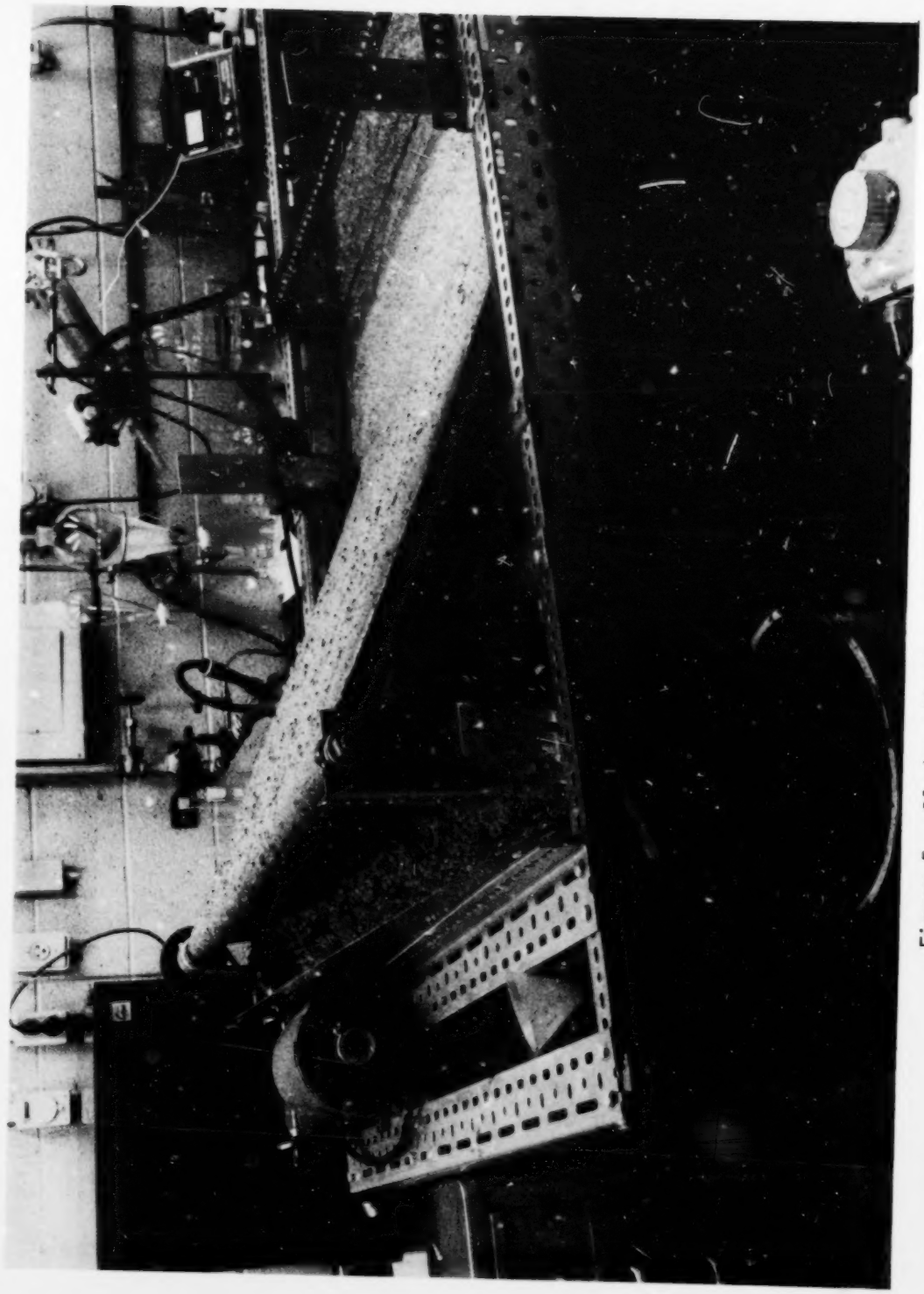

Figure 5. Sludge skimming apparatus

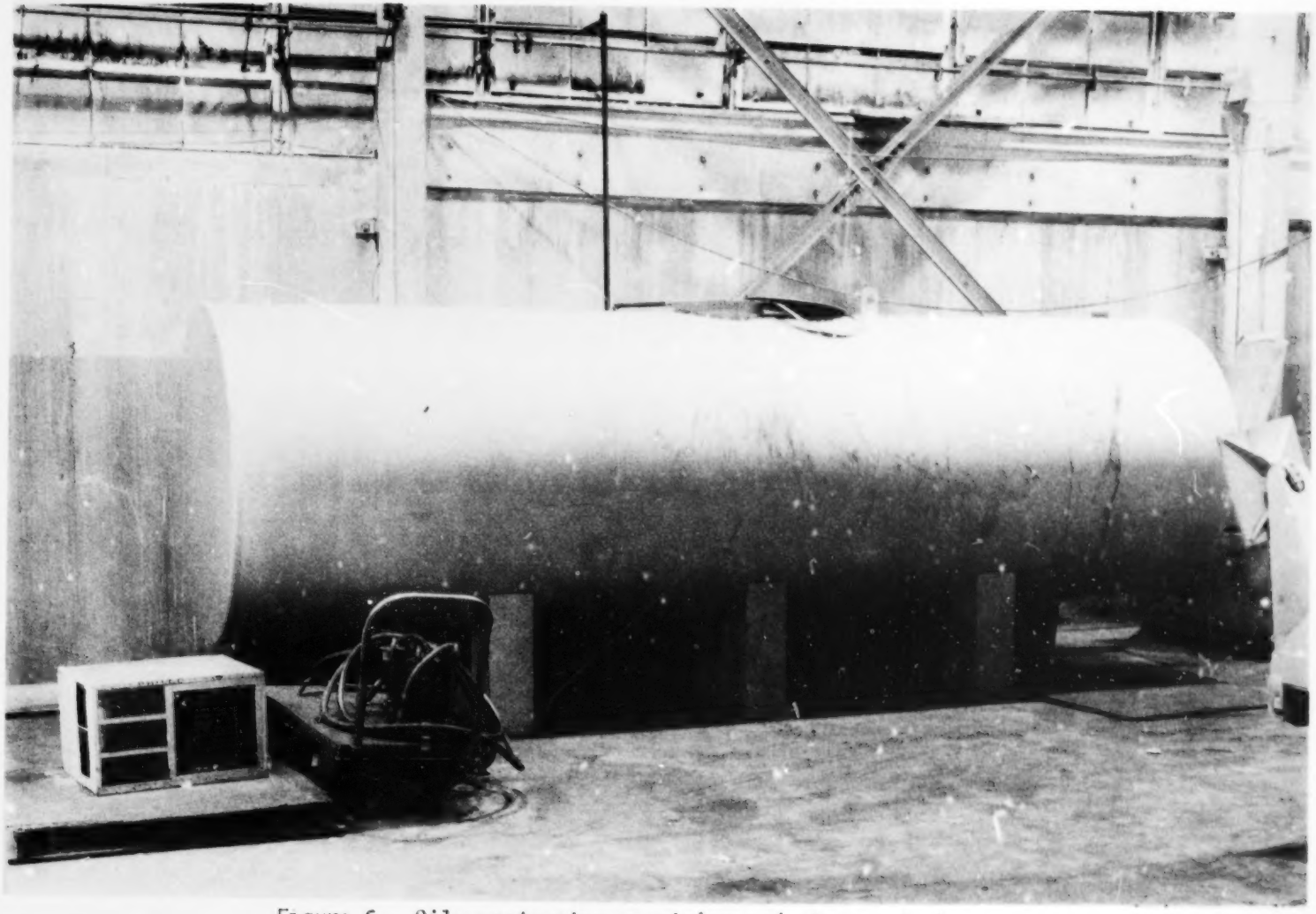

Figure 6. Oily wastewater receiving and storage tank

TABLE 1. STEADY-STATE MEASUREMENT IN THE ELECTROLYTIC CELL

Time, hr.	Turbidity (at distance past cathode), NTU				
	5 cm	45 cm	100 cm	150 cm	exit
0	2500	2500	2500	2500	2500
3	540	270	180	130	150
4	45	47	22	23	13
5	26	28	23	17	5
6	26	19	17	10	5
7	16	15	15	11	6
8	19	14	12	8	6

have a holding time of only one day, the biocidal treatment with bleach and cupric chloride was no longer necessary. As before, the wastewater was analyzed for pH, conductivity, turbidity, Freon extractables, solids, and anionic surfactants. In addition, a one liter sample of the wastewater was treated electrolytically in a beaker to determine the proper setting of the operating parameters for effective treatment. This was done by adding an amount of salt to the wastewater to give the desired conductivity, setting the current at 0.5 amp and observing the time required to just break the emulsion. The results were used to calculate the concentration of iron which is necessary to break the emulsion. The flow rate and current in the pilot unit were then set to give the same iron concentration.

The electrolytic unit has been operated with a single set of electrodes and provided with air bubblers for oxidation and flotation of the sludge. During a run the current, voltage, pH, conductivity, wastewater flow rate, and turbidity are checked and, if necessary, adjusted every hour. After 6-8 hours, when steady state conditions are reached, samples of the effluent and floating sludge are collected for analyses.

During most of the program period the floating sludge was removed by a belt skimmer at the end of the unit. In April, 1978 a dissolved air flotation unit was installed to improve the flotation of the sludge and reduce the level of suspended solids in the effluent. The unit is a Komline-Sanderson pilot flotation unit, model HR/SR-1. (Komline-Sanderson Corp., Peapack, NJ). The flotation area is 929 cm^2 (1 ft^2).

Dissolved Air Flotation (DAF) is a liquid-solid separation process that takes advantage of the fact that if air is dissolved in water under pressure, and the pressure is later released, the dissolved air will be released from solution in the form of vast numbers of minute bubbles. Actual flotation occurs when these bubbles become attached to suspended solid particles, oils, or immiscible liquids, thus increasing their buoyancy and causing them to rise to the surface of the liquid in which they are suspended. Floated material is skimmed from the surface, and the clarified liquid overflows from the rear of the unit.

SECTION 4

RESULTS AND DISCUSSION

ANALYSIS OF PLANT EFFLUENT

Oily wastewater from the Livonia Transmission Plant is usually white in color with some tramp oil and scum floating on top. Occasionally, the color of the wastewater may be gray, the result of excess free oil and dirt. The wastewater has a mild odor of machine oil which sometimes turns rancid upon standing. This rancid odor is caused by a bacterial reaction which releases hydrogen sulfide. Details of the composition, bacterial reactions and general comments relating to cutting fluids can be found in References 4, 5, and 6.

The Livonia Transmission Plant represents one of the most varied machining operations that would be encountered in the industry. The Livonia plant does drawing, broaching, grinding, machining etc. on various cast iron, aluminum, and steel compositions. As a result of this, the wastewater is one of the most complex to treat. The major components of the wastewater are emulsified ("soluble") oils, surfactants, and tramp oils. In addition, it sometimes contains hydraulic oils, drawing compounds, transmission fluids, etc. The chemical composition and physical characteristics of the plant effluent change frequently and unpredictably.

Samples of the plant effluent were analyzed for oil by Freon extraction (Freon extractables), turbidity, anionic surfactants, pH, and conductivity and periodically for dissolved and suspended solids. In the first nine months of the program the batches were collected from a wet well just before the wastewater treatment plant. In the following 8 months the batches were collected from a process sewer line which leads to the wet well. Unless otherwise indicated, the tests were performed according to procedures recommended by the U.S. Environmental Protection Agency (7). The results of the analyses of over 80 samples, which were subsequently used in the evaluation of the electrolytic pilot unit, are presented in Table 2.

Freon Extractables

Freon extractables ranged from 313 ppm to 7164 ppm and averaged 1822 ppm with standard deviation of 1370 ppm. It is comprised mostly of soluble oil and surfactant, and some tramp oil. Occasionally it may include hydraulic oils, drawing compounds, etc.

Turbidity

The average turbidity as measured in Nephelometer Turbidity Units or NTU's (Model 2424 Analytical Nephelometer, Hach Chemical Company, Ames, Iowa) was 1780 NTU with standard deviation of 1280 NTU. The minimum turbidity was 300 NTU and

TABLE 2. ANALYSES OF UNTREATED WASTEWATER

Date	Freon extractables ppm	Turbidity NTU	Anionic surfactants ppm	pH	Conductivity $\mu\Omega^{-1}$ cm^{-1}
12-16-76	1300	880	-	9.4	870
02-01-77	864	1200	-	7.3	1040
02-11-77	3771	3300	250	9.1	1090
03-08-77	4973	3800	-	9.1	3000
03-28-77	3110	1600	75	9.6	1100
04-04-77	1075	1250	-	9.0	950
06-15-77	7164	3250	-	10.2	1080
06-21-77	2004	920	-	7.8	840
06-29-77	5178	2700	-	8.0	700
08-09-77	2300	970	70	8.1	940
10-03-77	1934	2700	-	9.5	1600
10-04-77	1326	2200	-	10.1	850
10-12-77	1850	2400	-	10.0	900
10-13-77	1414	1900	-	9.6	1500
10-18-77	3253	4300	-	9.4	800
10-19-77	3058	5500	-	9.8	870
10-20-77	1230	1750	-	9.3	850
10-21-77	2451	3000	-	9.6	480
10-25-77	848	1100	224	10.1	610
10-26-77	2980	3500	247	10.0	500
11-01-77	870	1150	121	10.1	900
11-03-77	2472	3300	285	10.6	1420
11-08-77	492	520	108	10.3	800

(continued)

TABLE 2. (continued)

Date	Freon extractables ppm	Turbidity NTU	Anionic surfactants ppm	pH	Conductivity $\mu\Omega^{-1}$ cm^{-1}
11-10-77	700	800	206	10.0	1250
11-22-77	708	1200	150	9.6	620
11-23-77	313	310	130	9.9	560
12-13-77	624	650	180	10.2	780
12-15-77	591	550	170	11.4	3300
12-19-77	375	300	120	10.3	750
12-20-77	664	450	90	10.3	800
01-09-78	736	800	170	9.9	1000
01-10-78	2369	2900	-	10.2	1350
01-11-78	1045	1200	120	10.2	1400
01-12-78	1450	1700	90	9.6	1100
01-13-78	704	900	95	9.8	1040
01-16-78	825	900	160	10.2	1200
01-17-78	557	550	95	10.2	1340
01-18-78	586	560	70	10.1	1050
01-19-78	1205	1100	280	9.7	1220
01-20-78	3328	2000	-	9.9	1280
01-26-78	3230	4500	-	9.8	750
01-30-78	622	600	-	9.6	650
01-31-78	2300	2000	-	9.2	750
02-01-78	1600	1900	-	9.7	750
02-02-78	1250	1500	-	9.9	900

(Continued)

TABLE 2. (continued)

Date	Freon extractables ppm	Turbidity NTU	Anionic surfactants ppm	pH	Conductivity $\mu\Omega^{-1}$ cm^{-1}
02-14-78	745	640	-	8.4	650
02-15-78	1004	1300	-	8.3	650
02-16-78	2544	2600	100	8.5	660
02-20-78	1725	1750	40	9.2	750
02-21-78	1708	2200	60	9.4	1000
02-22-78	1331	1750	45	9.1	950
02-23-78	5388	5200	130	8.9	850
02-24-78	4984	4900	150	8.0	850
02-25-78	3154	5300	90	8.0	950
02-26-78	2050	2400	90	7.5	750
02-27-78	1260	1150	40	8.2	750
02-28-78	1117	950	25	8.8	1450
03-01-78	1071	1200	30	8.7	700
03-02-78	2538	2000	35	8.5	750
03-03-78	1270	1150	45	8.6	770
03-09-78	935	1000	50	8.6	680
03-10-78	1296	1200	60	8.9	950
03-13-78	1956	1500	55	9.2	880
03-14-78	1444	800	35	9.2	1000
03-15-78	3315	1900	60	9.2	1150
03-16-78	1342	1200	45	9.2	1050
03-17-78	1200	1300	50	9.0	780
03-20-78	900	750	-	8.6	600

(continued)

TABLE 2. (continued)

Date	Freon extractables ppm	Turbidity NTU	Anionic surfactants ppm	pH	Conductivity $\mu\Omega^{-1}$ cm^{-1}
03-21-78	970	1100	-	8.4	600
04-06-78	826	620	50	9.9	950
04-11-78	1305	1400	70	9.8	860
04-12-78	1102	780	40	10.3	900
05-02-78	968	720	35	10.6	1000
05-03-78	1526	770	40	10.1	1050
05-04-78	1217	870	30	10.3	1080
05-05-78	2230	1600	45	10.0	860
05-11-78	1186	1000	30	10.4	850
05-23-78	1361	1400	45	9.7	740
05-24-78	3218	2900	80	9.5	800
05-25-78	3842	4200	90	10.4	1200
$\bar{x}$	1822	1780	102	9.3	963
σ	1370	1280	70	1.4	469

the maximum 5500 NTU. The turbidity correlates relatively well with Freon extractables with a correlation coefficient of 0.79.

Anionic Surfactant

The surfactants in the wastewater are mainly petroleum sulfonates (sodium salt) and carboxylates which are used to stabilize the oil-in-water emulsion and in washing operations. The average concentration of the anionic surfactants was 102 ppm with a standard deviation of 70 ppm. The maximum value was 285 ppm and the minimum 25 ppm.

pH

The pH of the plant wastewater varied between 7.3 and 11.4. The average pH was 9.3 with standard deviation of 1.4.

Conductivity

The conductivity of the wastewater varied between 480 and 3300 μmho/cm. The average conductivity was 963 μmho/cm.

Dissolved Solids

The dissolved solids are comprised mainly of the inorganic salts in the wastewater. The dissolved solids, which contribute to the conductivity of the effluent, ranged between 750 and 1160 ppm and averaged 1000 ppm for the few runs analyzed.

Suspended Solids

The suspended solids, comprised of dirt, fine metallic particles, scum, paper particles, etc., ranged between 300 and 460 ppm. The suspended solids tend to stick to the walls of pipes, flowmeter and pumps eventually leading to reduced and inconsistent flow rates

OPERATING PARAMETERS

The operating parameters which were monitored and controlled during the experimental runs are current, flow rate, pH, and type and concentration of salt. These parameters were adjusted according to the influent compositions with the major objective of obtaining an effective treatment at a minimum cost and with the generation of a sludge with as little iron content as possible. A second objective was to assess the influence of these variables on treatment effectiveness. The operating conditions of the experimental runs conducted in the program are presented in Table 3 along with the quality of the treated effluent.

Current

The current has the most pronounced effect on the treatment of the oily wastewater. It is also the most convenient variable to control. For a given influent composition and flow rate the current determines the rate of iron dissolution (assuming no anodic passivation) and, thereby, the ratio of iron to oil. Throughout this program

TABLE 3. SUMMARY OF OPERATING CONDITIONS AND EFFLUENT QUALITY

Influent		Operating conditions						Effluent quality			
Date	Freon extractables ppm	Flow rate l/min	Salt concentration Normality	pH	Current amp	Voltage volt	Conductivity $\mu\Omega^{-1}$ cm^{-1}	Freon extractables ppm	Turbidity NTU	Surfactant ppm	Dissolved solids ppm
12-16-76	1300	3.8	0.01N NaCl	8.1	35	18	1750	22	5	-	-
02-01-77	864	3.8	"	7.0	20	8	2200	-	330	-	-
02-11-77	3771	1.9	"	7.3	35	13	2200	230	170	-	-
03-08-77	4973	1.9	0.02N $CaCl_2$	8.3	35	12	1650	16	2	-	-
03-28-77	3110	3.8	0.01N NaCl	7.8	35	10	2200	8	115	20	1480
04-04-77	1075	3.8	0.01N $CaCl_2$	7.3	25	11.5	1900	5	1	-	-
06-15-77	7164	1.9	"	6.9	35	12	2100	71	110	-	-
06-21-77	2004	3.8	0.01N NaCl	7.5	35	11	2200	18	8	-	-
06-29-77	5178	3.8	0.01N $CaCl_2$	6.9-	25	11	1600	11	12	-	-
08-09-77	2300	3.8	"	7.0	25	16	2000	10	7	1	-
10-03-77	1934	3.8	"	7.0	30	6	2800	281	570	-	-
10-04-77	1326	3.8	"	6.8	30	8	2000	5	3	-	1200
10-12-77	1850	3.8	"	7.0	30	8	2000	-	650	-	-
10-13-77	1414	3.8	"	9.0	30	8	2000	-	440	-	-

(continued)

TABLE 3. (continued)

Influent		Operating conditions						Effluent quality			
Date	Freon extractables ppm	Flow rate l/min	Salt concentration Normality	pH	Current amp	Voltage volt	Conductivity $\mu\Omega^{-1}$ cm^{-1}	Freon extractables ppm	Turbidity NTU	Surfactant ppm	Dissolved solids ppm
10-18-77	3253	3.8	0.01N $CaCl_2$	6.8	35	14	1700	-	390	-	-
10-19-77	3058	1.9	"	6.2	35	16	1750	15	9	-	1180
10-20-77	1230	3.8	"	6.8	30	16	1430	16	9	-	1610
10-21-77	2451	3.8	.01N NaCl	6.8	35	16	1450	286	440	-	-
10-25-77	848	1.9	.01N NaCl	6.7	35	14	1900	35	40	-	1000
10-26-77	2980	3.8	.01N $CaCl_2$	7.5	35	18	1580	9	8	-	1260
11-01-77	870	3.8	"	9.8	20	12	1450	61	110	-	930
11-03-77	2472	1.9	"	9.6	30	12	1690	13	14	-	980
11-08-77	492	3.8	"	10.1	30	14	1400	13	2	-	990
11-10-77	700	3.8	"	9.7	25	14	1400	8	2	-	880
11-22-77	708	3.8	0.01N $CaCl_2$	9.4	20	12	1500	11	1	-	1070
11-23-77	313	3.8	"	9.6	20	14	1250	6	1	-	1220
12-13-77	624	7.6	"	9.9	30	13	1350	190	90	-	1080
12-15-77	591	1.9	0.02N $CaCl_2$	11.3	35	11	3400	145	140	90	2020

(continued)

TABLE 3. (continued)

Influent		Operating conditions						Effluent quality			
Date	Freon extractables ppm	Flow rate l/min	Salt concentration Normality	pH	Current amp	Voltage volt	Conductivity $\mu\Omega^{-1}$ cm^{-1}	Freon extractables ppm	Turbidity NTU	Surfactant ppm	Dissolved solids ppm
12-19-77	375	3.8	0.01N $CaCl_2$	10.1	30	14	1300	7	1	20	920
12-20-77	664	3.8	"	9.7	25	14	1220	7	6	12	780
01-09-78	736	3.8	"	9.3	25	13	1400	14	4	-	-
01-10-78	2369	3.8	"	9.6	35	14	1700	122	215	-	-
01-11-78	1045	3.8	"	9.8	35	14	1850	31	4	-	-
01-12-78	1450	3.8	"	9.6	30	12	1600	8	10	-	-
01-13-78	704	1.9	"	9.3	12	13	1650	14	3	-	-
01-16-78	825	3.8	"	9.8	20	9	1650	12	4	-	-
01-17-78	557	3.8	0.005N $CaCl_2$	9.9	10	6	1400	32	13	-	-
01-18-78	586	3.8	0.01N $CaCl_2$	9.6	10	5	1780	9	4	-	-
01-19-78	1205	3.8	"	9.4	20	9	1500	27	8	-	-
01-20-78	3328	---------- Pump Failure ----------						---------- Pump Failure ----------			
01-26-78	3230	3.8	0.01N $CaCl_2$	9.0	30	17	1350	-	110	-	-
01-30-78	622	3.8	"	8.7	15	6	1400	10	5	-	-

(continued)

TABLE 3. (continued)

Influent		Operating conditions						Effluent quality			
Date	Freon extractables ppm	Flow rate l/min	Salt concentration Normality	pH	Current amp	Voltage volt	Conductivity $\mu\Omega^{-1}$ cm^{-1}	Freon extractables ppm	Turbidity NTU	Surfactant ppm	Dissolved solids ppm
01-31-78	2300	3.8	0.01N $CaCl_2$	8.4	30	16	2000	10	7	1	-
02-01-78	1600	3.8	"	8.6	30	12	1400	18	5	-	-
02-02-78	1250	3.8	"	9.2	25	15	1400	8	5	-	-
02-14-78	745	3.8	"	8.2	20	9	1450	4	4	-	-
02-15-78	1004	3.8	"	8.1	30	13.5	1200	8	3	-	-
02-16-78	2544	3.8	"	8.2	35	17	1300	15	3	-	850
02-20-78	1725	3.8	0.01N NaCl	9.3	35	11	1850	-	140	-	-
02-21-78	1708	3.8	0.01N $CaCl_2$	9.3	35	12	1950	36	150	-	-
02-22-78	1331	3.8	"	9.1	35	12	1900	37	90	-	1810
02-23-78	5308	1.9	"	8.0	30	9	1600	20	13	-	-
02-24-78	4984	1.9	0.02N $CaCl_2$	7.2	30	11	2500	5	8	-	1760
02-25-78	3154	----------Pump Failure ----------						----------Pump Failure ------			
02-26-78	2050	3.8	0.01N $CaCl_2$	6.7	25	19	1720	7	5	-	-
02-27-78	1260	3.8	"	8.0	25	22	1550	8	8	-	-

(continued)

TABLE 3. (continued)

Influent		Operating conditions						Effluent quality			
Date	Freon extractables ppm	Flow rate l/min	Salt concentration Normality	pH	Current amp	Voltage volt	Conductivity $\mu\Omega^{-1}$ cm^{-1}	Freon extractables ppm	Turbidity NTU	Surfactant ppm	Dissolved solids ppm
02-28-78	1117	3.8	0.01N $CaCl_2$	8.6	25	25	1800	11	4	-	1520
03-01-78	1071	3.8	"	8.5	25	39	1470	4	2	-	1860
03-02-78	2538	3.8	"	8.1	25	27	1800	10	7	-	1420
03-03-78	1270	3.8	"	8.2	35	27	1670	17	12	-	1640
03-09-78	935	3.8	"	7.8	15	7	1560	10	4	-	-
03-10-78	1296	1.9	"	8.0	12.5	6	1680	15	43	-	910
03-13-78	1956	3.8	"	8.5	20	8	1520	7	6	-	1290
03-14-78	1444	3.8	"	8.5	10	5	1760	14	5	-	1390
03-15-78	3315	3.8	"	8.0	25	10	1850	15	37	-	1250
03-16-78	1342	1.9	"	8.2	10	5	1650	8	5	-	890
03-17-78	1200	---------- Pump Failure ----------						--------- Pump Failure ----------			
03-20-78	900	3.8	0.01N $CaCl_2$	8.2	20	12	1650	18	12	-	-
03-21-78	970	3.8	"	8.0	20	13	1400	-	60	-	-
04-06-78	826	3.8	"	9.2	20	10	1650	12	7	-	-

(continued)

TABLE 3. (continued)

Influent		Operating conditions						Effluent quality			
Date	Freon extractables ppm	Flow rate l/min	Salt concentration Normality	pH	Current amp	Voltage volt	Conductivity $\mu\Omega^{-1}$ cm^{-1}	Freon extractables ppm	Turbidity NTU	Surfactant ppm	Dissolved solids ppm
04-11-78	1305	3.8	0.01N $CaCl_2$	8.8	20	11	1450	-	9	-	-
04-12-78	1102	3.8	"	8.5	20	11	1400	13	68	-	890
05-02-78	968	3.8	"	8.4	20	13	1350	17	30	-	-
05-03-78	1526	3.8	"	8.3	20	13	-	104	340	-	-
05-04-78	1217	3.8	"	8.4	35	19	1450	22	120	-	-
05-05-78	2230	3.8	"	8.5	35	17	-	32	120	-	-
05-11-78	1186	3.8	"	9.0	35	20	1500	-	6	-	-
05-12-78	Batch of 05-11-78	3.8	"	9.0	35	22	-	12	14	-	-
05-23-78	1361	3.8	"	8.7	30	20	-	69	65	-	-
05-24-78	3218	3.8	"	8.7	35	11	1600	25	8	-	-
05-25-78	3842	3.8	"	9.1	35	12	1500	28	30	-	-
$\overline{X}$ total								35	70		1257
$\overline{X}$ $CaCl_2$								27	60		

current adjustment was primarily relied upon to obtain effective treatment. Only with difficult-to-treat batches, where maximum operating current was not sufficient at the usual flow rate of 3.8 l/min, were other parameters such as flow rate or salt concentration adjusted. Maximum operating current is limited by the onset of excessive oxygen evolution at the anode at the expense of iron dissolution. This occurs at current density of 10 mA/cm^2 of projected electrode which for the exposed electrode dimensions used (3820 cm^2) corresponds to 38 A.

In this program the current ranged between 10 and 35 A. The current used in each case was the minimum required to break the emulsion as determined by visual observation of the change in turbidity. Usually the flow rate was at the design value of 3.8 l/min, however, in several cases the flow rate was reduced to 1.9 l/min resulting in an equivalent current of twice that for standard conditions.

The average current required for effective treatment was 31.5 A (adjusted to 3.8 l/min) with standard deviation of 15.6 A. Generally, the required current was found to increase with the influent oil concentration. But as mentioned previously the proper setting of the current for effective treatment was determined by a beaker test.

The beaker test was found to be useful because our experience at the Livonia Transmission Plant has shown that knowledge of the concentration of oil and surfactants in the wastewater may not always be sufficient to establish the proper operating conditions, since other unidentified components in the plant wastewater may effect the performance of the electrolytic cell. Therefore, simple correlations, which would predict the setting of the operating parameters with certainty based on influent properties, could not be established. While this situation may be true at the Livonia Transmission Plant where wastewater is received from a large number of diversified operations, it is likely that in other plants, where the composition of wastewaters remains fairly constant, simple correlations could be established. In any event, a feedback control based on effluent quality may be feasible. This is discussed in a later section.

Operating Voltage

The voltage across the electrode was found to depend on the current, the conductivity of the wastewater, and the extent of anodic fouling. Generally, the voltage varied between 5 and 30 volts and averaged 13 volts. In some instances the operating voltage increased to 40 volts or more due primarily to anode fouling. In these cases the tests were stopped and corrective measures were taken to reduce the voltage to normal levels. A detailed discussion of voltage increase is presented later in conjunction with the durability studies.

Based on the data of current and voltage, the average electrical energy consumption for the electrolytic dissolution of iron was calculated to be 5.76 MJ/m^3 (1.6 $kW\text{-}hr/m^3$; 6 kW-hr/1000 gal) of wastewater for the range of oil concentrations encountered. The calculation was based on the use of 0.01N CaCl and flow rate of 3.8 l/min.

pH Effects

To study the influence of pH on the performance of the electrolytic cell two sets of experiments were conducted. One set of experiments was conducted to determine

the influence of pH on the rate of iron dissolution, the other to compare the performance of the electrolytic cell with and without pH adjustment of the influent.

To study the effect of pH on the rate of electrolytic dissolution of iron the cell was filled with clean tap water and the pH adjusted to a desired value. The electric power was turned on at a specified current and the water recirculated in the cell. The concentration of iron in the water was determined hourly over a period of 5 hours. The data were used to calculate the rate of iron dissolution in ppm/hr. The results, presented in Table 4, show that pH does not affect the rate of electrolytic dissolution of iron. It should be noted that this is true only as long as the cell operates below the limiting current density.

TABLE 4. IRON DISSOLUTION RATE

pH	Iron dissolution rate ppm/hr	
	25 amp	35 amp
6	15	21
10	15	19

To evaluate the influence of pH on the performance of the electrolytic cell, large batches of wastewater were collected in the storage tank. Each batch was treated in the electrolytic cell with and without pH adjustment, while maintaining other operating parameters constant. A direct comparison of the Freon extractables is shown in Table 5 along with detailed operating conditions. These runs indicate that pH adjustment may not be necessary for effective treatment of the plant wastewater. Subsequent experimental runs have, in fact, shown that the electrolytic cell performs well without adjusting the pH of the influent, which simplifies and reduces the cost of the process.

Salt Effects

The main purpose of salt addition is to avoid passivation of the iron chips and increase the conductivity of the wastewater, thereby reducing power consumption. In addition, the type and concentration of salt influences the effectiveness of the electrolytic treatment. It is known, for example, that bi- and tri- valent salts, because of their high ionic strengths, are much more active in destabilizing and breaking emulsions than mono-valent salts (8). An increase in concentration also affects emulsion breaking.

In this program two salts were evaluated: sodium chloride and calcium chloride. Sodium chloride is preferable economically, however, calcium chloride is preferable with respect to treatment effectiveness. This feature is particularly noticeable with batches of wastewater which are difficult to treat electrolytically.

Most of the runs listed in Table 3 were done with $CaCl_2$. In a few cases, NaCl permitted fairly adequate treatment. In cases where it did not, the full run was not made with NaCl, but with $CaCl_2$.

TABLE 5. RESULTS OF TREATMENT OF PLANT WASTEWATER WITH AND WITHOUT pH ADJUSTMENT

Freon extractables before treatment ppm	Salt concentration N	Anionic surfactant ppm	Anionic surfactant % of Freon extractables	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm
2980	$CaCl_2$, 0.01 N	247	8.3	7.5	3.8	35	18	8	9
				10	3.8	35	20	5	18
870	$CaCl_2$, 0.01 N	121	13.9	7.1	3.8	35	21	135	210
				10	3.8	20	12	110	61
2472	$CaCl_2$, 0.01 N	285	11.5	7.1	1.9	30	15	10	13
				9.6	1.9	30	12	14	13
492	$CaCl_2$, 0.01 N	108	22.0	10	3.8	30	14	4	14
700	$CaCl_2$, 0.01 N	206	29.4	7.2	3.8	25	19	11	10
				9.7	3.8	25	14	6	8
664	$CaCl_2$, 0.01 N	90	13.5	10.3	3.8	25	14	6	7
				7.0	3.8	25	13	3	9

Electrolytic treament of plant wastewater in a 1-liter beaker has also shown the superiority of $CaCl_2$. For example, a batch of 2-21-78 could not be broken after 18.5 minutes at 0.5 A using 0.01N NaCl but with 0.01N $CaCl_2$ an effective treatment resulted within 16 min. In another beaker study (2-23-78) it took 44 minutes at 0.5 A to break the emulsion using 0.01N NaCl, but with 0.01N $CaCl_2$ it took only 24 minutes.

Laboratory tests have shown that $CaCl_2$, $FeSO_4$, $AlCl_3$, and $CuSO_4$ precipitate the surfactant out of solution but NaCl does not, which provides partial explanation to the activity of $CaCl_2$.

Based on a large number of observations it appears that the optimum concentration of $CaCl_2$ is 0.01N. On some occasions when surfactant concentration is quite high and the treatment is difficult, a larger dosage of $CaCl_2$, possibly 0.02N, may be necessary to obtain effective treatment. But these cases are rare.

The use of $CaCl_2$ with high flow rates of air through the bubblers results in a build-up of scale on the cathode which appears to be mainly deposits of insoluble calcium compounds. Metal analysis of these deposits show that Ca comprises 29% by weight. These deposits are easily removed by brushing. Also, the rate of deposit build-up can be controlled to some extent by reducing the flow of air through the bubblers.

EFFLUENT QUALITY

The electrolytically treated wastewater was sand filtered to remove suspended matter, then analyzed for Freon extractables, turbidity, surfactants and dissolved solids. Occasionally, BOD and suspended solids were determined. The effluent quality results are tabulated in Table 3 along with the influent oil concentration and operating conditions.

Freon Extractables

The measured Freon extractables of the treated wastewater, the criterion of treatment effectiveness, ranged from 4 to 286 ppm (Table 3). For those runs for which there is Freon extractable data (not including the 7.6 l/min run which is over the design capacity), the average was 35 ppm. Excluding the NaCl runs, Freon extractables averaged 27 ppm--95% were below 100 ppm (adequate for discharge to large municipal sewer systems); 90% were below 50 ppm; 83% were below 25 ppm (adequate for discharge to smaller municipal sewer systems); 62% were below 15 ppm; and 36% were below 10 ppm (this value or lower required for discharge to navigable waters).

Since the cell was operated at a current to generate the iron concentration to just achieve demulsification, the Freon extractables may be somewhat higher than required for some discharges. Higher current generally results in lower Freon extractables. This effect is illustrated in Figure 7 which shows the effluent Freon extractables as a function of the ratio of dissolved iron to influent oil--each set of points is a single batch of waste water.

A few runs essentially were untreatable even for large municipal sewer system discharge on a single pass through the cell. Theoretically, the introduction of more iron should reduce the levels of Freon extractables. However, this may not be true in all cases since unexpected substances such as high concentrations of bacteria or

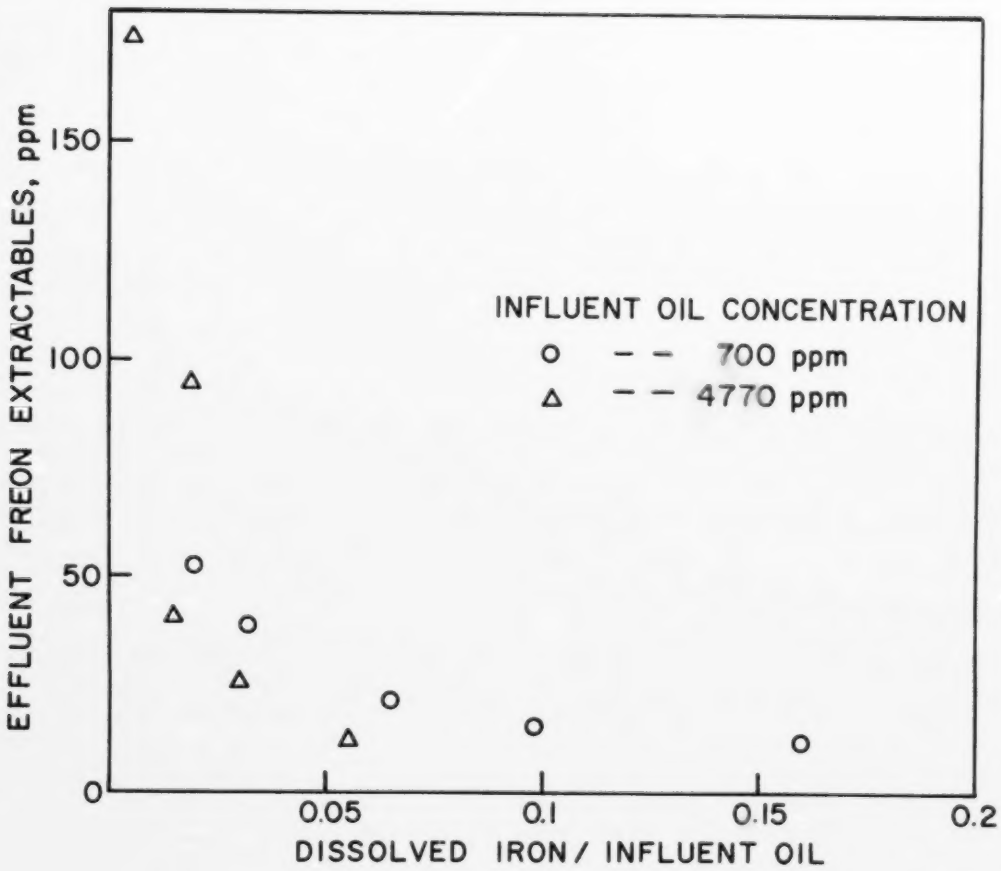

Figure 7. Effect of iron to oil weight ration on effluent oil content

transmission fluid additives may tend to enhance the emulsion stability or selectively adhere to or react with the iron rendering it less active.

The presence of small amounts of bacteria does not significantly influence the operation of the electrolytic cell; however, if the wastewater is allowed to stand, it will turn rancid with the formation of hydrogen sulfide and the generation of a biological growth. This resulting wastewater is more difficult to treat than the original since hydrogen sulfide presumably precipitates some of the iron as iron sulfide. Also, the Freon extractable value may be in error as to the concentration of oil because the Freon-water interface is virtually non-existant.

Turbidity

The turbidity of the electrolytically treated and sand filtered wastewater ranged between 1 and 650 NTU and averaged 60 NTU (excluding NaCl runs and the 7.6 l/min run). The turbidity results from remaining emulsified oil and fine suspended particles (mostly iron hydroxide). The turbidity was found to have a positive correlation with Freon extractables with a correlation coefficient of 0.88. As will be discussed later on this feature may be used for automatic feed back control.

Surfactants

The concentration of anionic surfactants in the treated water ranged between 1 and 90 ppm. When the treatment was effective the concentration of surfactants was 20 ppm or less. Higher concentrations, accompanied by foaming in the cell, were observed when the treatment was only partially effective.

BOD

A few tests of biological oxygen demand (BOD) indicated that 5 day BOD value of the treated wastewater is about 90 ppm.

Dissolved Solids

The effluent dissolved solids varied between 780 and 2020 ppm. The average was 1257 ppm with standard deviation of 346. The process adds a maximum of 550 ppm to what is present in the influent. By comparison, conventional methods with chemicals generally add about 2,000-3,000 ppm of dissolved solids.

Suspended Solids

Prior to the use of the dissolved air flotation unit or sand filter the suspended solids, comprised mainly of iron hydroxide, ranged between 600 and 2240 ppm. It was observed that the concentration of suspended solids depends on the floating ability of the iron hydroxide-air sludge. In most cases the oily sludge, generated when treating actual plant wastewater, did not float well without forced flotation.

When the dissolved air flotation unit was used to force flotation of the sludge the concentration of suspended solids in the processed wastewater ranged between 25 and 135 ppm. Sand filtered wastwater had a negligible amount of suspended solids. This will be discussed in more detail later in the report.

DURABILITY STUDIES

The objectives of the durability studies were to evaluate the performance of the cell under uninterrupted-continuous operation, to identify any operational problems, and to alleviate any potential problem areas.

The durability tests were conducted as follows: About 5.6 m^3 (1500 gal) of wastewater were pumped into the storage tank and analyzed for pH, conductivity, turbidity, Freon extractables, and anionic surfactants. In addition, a 1 liter sample of the wastewater was treated electrolytically at an iron chip anode in a beaker to determine the initial setting of the operating conditions. The procedure for the beaker test is described in the Experimental section.

During the durability test the treated wastewater was analyzed for pH, conductivity, turbidity, and Freon extractables, and the operating conditions were adjusted for minimum iron and minimum sludge formation. Minor maintenance work, which did not disrupt the test, such as the addition of iron chips and brushing between the electrodes, was also performed. When the supply of wastewater in the storage tank was low, a new batch of about 5.6 m^3 was pumped to the storage tank. In this manner, the electrolytic cell operated 24 hours a day without interruption.

During the program period five durability tests have been conducted. Each test started with new iron chips and clean electrodes. The results of the five durability tests are presented in Tables 6 thru 10. These results show that, when the electrodes are kept clean, the electrolytic cell provides efficient treatment. Also encouraging is the fact that the rise in the operating voltage is not as rapid as was experienced in the first part of the program with interrupted runs.

The major operational problem is the accumulation of oily sludge in the anodic chip cage and in the space between the anode and cathode which restricts the flow of wastewater through the electrodes. Eventually, the electrodes become completely blocked, the influent flows over the iron chips, and the performance of the cell decreases substantially.

It was found that brushing and purging with air between the electrodes to remove the accumulated sludge alleviates this problem temporarily. To date we were able to operate the cell continuously up to 14 days.

First Durability Test

The first durability test is summarized in Table 6. The test lasted 11 days and used about 60 m^3 (16,000 gal) of wastewater. Throughout the test the space between the electrodes was brushed several times a day to reduce the rate of sludge accumulation. After 11 days the test was discontinued because of excessive accumulation of sludge which blocked the flow of wastewater through the anode.

Second Durability Test

The test, summarized in Table 7, continued for 8 days and consumed about 27 m^3 (7200 gal) of wastewater. As in the first test frequent brushing between the electrodes was necessary to avoid rapid sludge accumulation in the electrodes, and the test was stopped for similar reasons.

TABLE 6. SUMMARY OF FIRST DURABILITY TEST

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
1-09-78	1:00pm	736	0.01	9.9	3.8	25	25	-	-	Beginning of test.
1-10-78	8:00am	"	0.01	9.6	3.8	25	14	4	14	Water level 1.3 cm higher upstream of electrodes. No sludge floating.
	10:00am	2369	0.01	9.6	3.8	35	14.5	-	-	Operating conditions adjusted for new batch.
	2:30pm	"	0.01	9.6	3.8	35	13	10	-	
1-11-78	8:00am	"	0.01	9.8	3.8	35	14	215	122	Water level 1.9 cm higher upstream of electrodes and overflowing chips. ½ cell covered with floating sludge.
	10:00am	1045	0.01	9.8	3.8	35	14	-	-	New batch of wastewater. Space between electrodes cleaned with brush to stop flow over chips.
	2:40pm	"	0.01	9.8	3.8	35	14	16	-	Water level equal on both sides of electrodes.
1-12-78	8:00am	"	0.01	9.8	3.8	35	14	5	31	Water level 2.2 cm higher upstream Electrodes cleaned with brush.
	9:00am	1450	0.01	9.6	3.8	30	12	-	-	Operating conditions adjusted for new batch.
	3:00pm	"	0.01	9.6	3.8	30	13	8	7	
1-13-78	10:00am	"	0.01	9.6	3.8	30	12	10	8	
	2:00pm	704	0.01	9.3	1.9	12	13	3	-	Operating conditions adjusted for running unit unattended through the weekend.

(continued)

TABLE 6. (continued)

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
1-16-78	8:00am	704	0.01	9.3	1.9	12	13	9	14	Water level 3.2 cm higher upstream Brushed between electrodes. Washed chips and added some fresh chips
	10:30am	825	0.01	9.8	3.8	20	10	-	-	Conditions adjusted for new batch.
	3:00pm	"	0.01	9.8	3.8	20	9	4	12	
	3:20pm	"	0.01	9.8	3.8	15	6.5	4	-	Reduced current due to excess Fe^{+3}.
1-17-78	8:00am	"	0.01	9.8	0.8	15	8	-	-	Pump slowed up during night.
	3:00pm	557	0.005	9.9	3.8	10	6	13	32	
1-18-78	8:30am	"	0.005	9.9	3.8	10	5	33	38	Water level 1.9 cm higher upstream White foam on water surface. No floating sludge.
	3:00pm	586	0.01	9.6	3.8	10	5	38	28	
1-19-78	8:30am	"	0.01	9.6	3.8	10	5	4	9	Electrodes were brushed.
	3:00pm	1205	0.01	9.4	3.8	20	9	8	27	
1-20-78	1:00pm	3328	0.01	9.9	1.9	15	6	-	-	Operating conditions adjusted for unattended run through weekend.
1-23-78	Pump failed during weekend. Test stopped.									

TABLE 7. SUMMARY OF SECOND DURABILITY TEST

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
1-26-78	10:00am	3230	0.01	9.0	3.8	30	10	-	-	Beginning of test.
	2:00pm	"	0.01	9.0	3.8	30	10	12	-	Floating sludge over 80% of cell.
1-27-78	9:00am	"	0.01	9.0	3.8	30	17	110	-	Electrodes cleaned with brush.
	2:30pm	"	0.01	9.0	1.9	15	6	90	-	Operating conditions adjusted for run through weekend.
1-30-78	8:00am	"								Flow of wastewater to cell stopped during the weekend because of pump instability.
	3:00pm	622	0.01	8.7	3.8	15	6	18	-	Test continued with a new batch.
1-31-78	9:00am	"	0.01	8.7	3.8	15	6	5	10	Water level higher upstream of anode. Electrodes brushed.
	4:00pm	2300	0.01	8.4	3.8	30	13	10	8	
2-01-78	8:20am	"	0.01	8.4	3.8	30	17	7	10	Water level higher upstream. Brushed electrodes. Added some iron chips
	3:30pm	1600	0.01	8.6	3.8	30	12	4	30	Electrodes brushed every 3 hours.
2-02-78	8:30am	"	0.01	8.6	3.8	30	12	5	18	Water level 1.9 cm higher upstream of electrode. Brushed between electrodes.
	3:30pm	1250	0.01	9.2	3.8	25	16	60	-	Electrodes brushed hourly.
2-03-78	8:30am	"	0.01	9.2	3.8	25	18	180	-	Wastewater flows over iron chips. Brushed between electrodes.
	1:00pm	"	0.01	9.2	3.8	25	15	5	8	Electrodes brushed hourly.
	2:00pm	Experiment stopped to improve electrodes design.								

TABLE 8. SUMMARY OF THIRD DURABILITY TEST

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
2-14-78	10:15am	745	0.01	8.0	3.8	15	8	-	-	Beginning of test.
	3:00pm	"	0.01	8.2	3.8	20	9	4	4	
2-15-78	8:30am	"	0.01	8.5	3.8	20	11	3	5	
	11:30am	1004	0.01	8.1	3.8	25	14	-	-	A new batch
2-16-78	8:00am	"	0.01	8.1	3.8	30	14	3	8	
	10:30am	2544	0.01	8.4	3.8	25	11.5	-	-	A new batch
	3:00pm	"	0.01	8.2	3.8	35	17	3	14	
2-17-78	8:00am	"	0.01	8.2	3.8	35	17	3	15.4	Test stopped because of excessive deposits on cathode.

TABLE 9. SUMMARY OF FOURTH DURABILITY TEST

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
2-23-78	1:00pm	5388	0.01	8.3	1.9	35	11	-	-	Beginning of test.
	3:15pm	"	0.01	8.0	1.9	30	9	13	20	
2-24-78	8:15am	"	0.001	8.2	1.9	30	17	560	-	$CaCl_2$ flow rate decreased overnight
	11:30am	4984	0.02	8.0	1.9	30	20	-	-	A new batch
2-25-78	9:30am	"	0.02	7.2	1.9	30	11	8	5	Electrodes brushed
	11:30am	3154	0.02	8.0	1.9	30	12	-	-	New batch
2-26-78	8:00am	"	-	-	-	-	-	1	-	Flow rate slowed to 0.4 l/min
	2:00pm	2050	0.01	7.5	3.8	25	12	-	-	A new batch
2-27-78	8:00am	"	0.01	6.7	3.8	25	19	5	7	Electrodes purged with air and brushed.
	12:30pm	1260	0.01	8.1	3.8	20	14	-	-	New batch
	3:30pm	"	0.01	6.7	3.8	25	18	13	16	
2-28-78	10:30am	"	0.01	6.4	3.8	25	22	8	8	Electrodes purged with air
	12:30pm	1117	0.01	8.6	3.8	25	23	14	-	New batch
	3:30pm	"	0.01	8.6	3.8	25	25	5	13	
3-01-78	8:30am	1117	0.01	8.6	3.8	25	25	4	11	Electrodes purged with air
	1:00pm	1071	0.01	8.5	3.8	25	30	-	-	New batch
	3:30pm	"	0.01	8.6	3.8	25	39	2	4	Electrodes purged with air
3-02-78	10:00am	"	0.01	6.8	3.8	16	44	7	13	Overvoltage. Electrodes brushed and purged with air. Iron chips worked with tap water. Added more chips.
	1:20pm	2538	0.01	7.8	3.8	25	17	10	-	New batch
	3:15pm	"	0.01	8.1	3.8	25	17	2	5	

(continued)

TABLE 9. (continued)

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
3-03-78	8:15am	2538	0.01	7.0	3.8	25	27	7	10.3	Electrodes purged with air
	1:00pm	1270	0.01	8.2	3.8	25	27	7	-	New batch
	3:15pm	"	0.01	8.0	3.8	35	27	12	17	
3-04-78	9:00am	"	0.01	8.0	3.8	22	44	-	-	Water overflowing electrodes. Overvoltage. Test stopped.

TABLE 10. SUMMARY OF FIFTH DURABILITY TEST

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
3-09-78	1:00pm	935	0.01	7.8	3.8	20	10	-	-	Beginning of test.
	3:30pm	"	0.01	7.8	3.8	15	6	1	-	
3-10-78	11:00am	"	0.01	7.0	3.8	15	7	4	9.5	Electrodes purged with air.
	3:15pm	1296	0.01	8.4	1.9	7.5	4	12	-	New batch.
3-11-78	9:00am	"	0.01	8.0	1.9	8	3.5	27	29	Electrodes purged with air.
3-12-78	10:30am	"	0.01	7.2	1.9	12.5	6	43	15	
3-13-78	8:20am	"	0.01	6.9	1.9	15	6	14	10.3	Electrodes purged with air.
	12:50pm	1956	0.01	8.7	3.8	20	7	18	-	New batch.
	3:00pm	"	0.01	8.5	3.8	20	8	8	3.4	
3-14-78	8:00am	"	0.01	7.7	3.8	20	7	6	7	Electrodes purged with air.
	12:20pm	1444	0.01	8.5	3.8	10	4	15	-	New batch.
	3:00pm	"	0.01	8.2	3.8	10	4.5	5	14	
3-15-78	11:00am	"	0.01	7.3	3.8	10	4.5	6	8.6	Electrodes purged with air.
	1:40pm	3315	0.01	8.3	3.8	20	9.5	6	-	New batch.
3-16-78	8:00am	"	0.01	8.0	3.8	25	9.5	37	15	Wastewater supply pump failed. Cell shut down temporarily.
	2:30pm	1342	0.01	8.2	1.9	10	5.5	28	-	New batch.
3-17-78	10:00am	"	-	8.2	-	10	5.5	5	8	Flow rate slowed to 0.8 l/min overnight.
	3:45pm	1200	0.01	8.5	1.9	10	4	-	-	New batch. Cell set to run unattended during weekend
3-20-78	9:00am	"	-	8.2	-	10	4	-	-	Pumps failed. No flow to cell. Electrodes brushed and purged with air.

(continued)

TABLE 10. (continued)

Date	Time	Influent oil concentration ppm	$CaCl_2$ concentration N	pH	Flow rate l/min	Current amp	Voltage volt	Turbidity NTU	Freon extractables ppm	Comments
3-20-78	3:00pm	900	0.01	8.2	3.8	20	13	-	-	New batch.
3-21-78	8:30am	"	-	8.1	-	20	11	1	5	Flow rate slowed to 1.9 l/min overnight.
	2:00pm	"	0.01	8.2	3.8	20	12	12	18	Electrodes purged with air.
	4:00pm	970	0.01	8.0	3.8	20	12.5	3	9	New batch.
3-22-78	8:30am	"	0.01	6.4	3.8	20	13	60	-	Electrodes purged with air.
	3:00pm	2050	0.01	8.6	3.8	35	23	90	-	New batch.
3-23-78	8:30am	"	0.01	8.4	3.8	35	32	2	5	Flow rate slowed to 2.3 l/min overnight.
										Test stopped -- long weekend.

The first two durability tests demonstrated that the accumulation of oily sludge in the anodic chip cage and in the space between the two electrodes can be a major operational problem. To reduce the rate of sludge accumulation in the space between the anode and cathode, the electrodes were redesigned. The cathode, which in the past extended above the water level, was shortened to about one centimeter below the water level to allow the oily sludge to float over it. In addition, pressurized air is bubbled in the space between the electrodes to provide turbulence and washing action, thereby minimizing the accumulation of sludge.

Third Durability Test

The test started with the new electrode design. To avoid accumulation of oily sludge air was bubbled continuously between the electrodes. The test was stopped after three days because of severe build up of insoluble calcium carbonate deposits on the cathode. Apparently, the continuous bubbling of air between the electrodes and the relatively high concentration of calcium ion resulted in a rapid build-up of $CaCO_3$ deposits. Results are given in Table 8.

Fourth Durability Test

To avoid the deposits of $CaCO_3$, it was decided to replace the $CaCl_2$ partially or completely with NaCl. This action, however, resulted in less effective treatment and it was necessary to return to $CaCl_2$ at a concentration of 0.01N.

The fourth durability test (Table 9) continued for nine days and used about 38 m^3 (10,000 gal) of wastewater. During the test the space between the electrodes was purged with air twice a day for 5 minutes and sometimes brushed. Accumulation of sludge between the electrodes was not observed. Also the $CaCO_3$ deposits on the cathode were light and did not interfere with the operation of the cell. Oily sludge did accumulate in the anodic cage leading, eventually, to elevated voltage and physical plugging of flow. In-situ washing of the iron chips with cold tap water for 10 minutes alleviated this condition temporarily.

Fifth Durability Test

The fifth durability test (Table 10) lasted 14 days and used about 57 m^3 (15,000 gal) of wastewater. During the test the space between the electrodes was purged with air twice a day and occasionally brushed. In addition the water upstream of the anode was continuously and vigorously agitated to maintain the influent well mixed and avoid separation of free oil droplets. This action appears to have also slowed the rate of plugging of the anode. Except for some pump failures the cell performed well throughout the test.

ELECTRODE PLUGGING

An increase in the operating voltage upon aging of the iron chips, was observed early in the program. During that time the cell was operating approximately 8 hours through the day and shut down for the night. After several days of operation the voltage usually exceeded the limit of the power supply, the chips had to be replaced, and the electrodes were steam cleaned.

An increase in the operating voltage was also observed during the durability tests, but at a slower rate. To determine what contributes to the rise in the voltage, the following experiments were conducted at the end of the fourth durability test when the operating voltage had increased to 44 volts.

In the first experiment the iron chips were replaced with new ones. The cell was filled with wastewater and the conductivity was adjusted to 1700 μ mho/cm, as at the end of the fourth durability test. When the power was turned on to 25 A the operating voltage was 25 volts. Thus replacing the iron chips reduced the operating voltage by 19 volts. In the next experiment the cathode was cleaned to remove oily and calcium deposits. This action had no effect on the operating voltage. Next, the anodic cage was cleaned with steam to remove oily deposits from the front face of the anode. This action brought the operating voltage down to 14 volts.

Thus, it appears, that the increase in the operating voltage is due primarily to accumulation of oily sludge in the anode cage.

As mentioned in the Experimental section, the front face of the anode is constructed of two layers: expanded titanium sheet and polyethylene screen. This type of construction appears to trap and accumulate oily sludge. By replacing the two-layer construction with a single titanium sheet with proper hole size, it may be possible to reduce the rate of sludge accumulation and extend the service life of the anode.

SLUDGE FLOTATION AND SLUDGE CHARACTERISTICS

The sludge generated by the electrolytic process is a mixture of water, oil, and iron hydroxide. Sludge flotation appears to depend on the ratio of iron to oil, the wastewater composition, and the type of assisted flotation equipment. During most of the program period, sludge flotation was effected by the use of porous membrane air bubblers which were located at the bottom of the cell. These bubblers were found to be somewhat deficient. Flotation requires the generation of fine air bubbles which adhere to the oily floc. If the bubbles are too large mixing instead of flotation may occur. In these experiments, the membrane properties changed with time and the bubble size changed from fine to larger bubbles. It should be noted that in laboratory experiments with simulated wastewater no difficulties were encountered in forcing the sludge to float with similar flotation equipment, and at about the same iron to oil ratio. Therefore, it seems that some components of the plant wastewater render the sludge more difficult to flocculate and to float. Indeed, the wastewater processed occasionally contained organic solvents, drawing compounds, grinding wheel resins, etc. Therefore, air bubbler flotation may be more effective with other wastewaters which may have simpler compositions.

In order to obtain a more effective sludge flotation, a dissolved air flotation unit (Komline-Sanderson model HR/SR-1) was installed. The treated wastewater was pumped at a rate of 3.8 l/min to the dissolved air flotation unit (D.A.F.) yielding a thick, easy to handle, floating sludge.

The performance of the D.A.F. is presented in Table 11. The unit removed from 86 to 98% of the suspended solids, and reduced iron concentration by as much as 97%. The average removal of suspended solids was 93%. Thus it appears that the sludge generated by the electrolytic process can be forced to float and that dissolved air

TABLE 11. EVALUATION OF THE PERFORMANCE OF THE DISSOLVED AIR FLOTATION

Date	Sampling location*	Turbidity NTU	Freon extractables ppm	Suspended Solids ppm	Iron Concentration ppm
5-02-78	1	800	-	679	110
	2	150	85	80	22
	3	30	17	nil	nil
5-03-78	1	1200	-	1595	110
	2	355	202	135	21
	3	340	104	-	-
5-04-78	1	650	-	840	95
	2	150	77	57	8.5
	3	120	22	-	-
5-05-78	1	1200	-	1122	140
	2	260	97	84	22
	3	120	32	-	-
5-11-78	1	690	-	1643	105
	2	57	74	25	7
	3	6	-	-	-
5-12-78	1	2400	-	2240	250
	2	50	31	40	7.5
	3	14	12	-	-
5-23-78	1	850	-	680	100
	2	120	113	33	5
	3	65	69	-	-
5-24-78	1	760	-	949	105
	2	70	89	131	6.5
	3	8	25	-	-
5-25-78	1	700	-	779	65
	2	80	56	57	3
	3	30	28	-	-

*1 - Before dissolved air flotation.
2 - After dissolved air flotation.
3 - After sand filtration

flotation is very effective for that purpose. If final polishing of the effluent through a sand filter is required to remove the last traces of suspended solids, the use of D.A.F. would substantially reduce the loading on the filter. In addition, the D.A.F. would occupy far less floor space than an air bubbler flotation system.

The sludge collected by the D.A.F. unit was analyzed to determine oil and water content. The sludge as received from the D.A.F. contained 6 to 12% oil, 86% water, and the balance insoluble solids. The total volume of generated sludge averages about 1 to 2% of the volume of wastewater treated. This volume is immediately decreased by a factor of two since about one-half of the water drains from the sludge within 30 minutes upon standing. If the sludge is permitted to stand overnight, then agitated, the water is not as readily drained from the sludge. This presumably is a result of entrained air being lost from the oil-iron floc and hydration of the iron hydroxide. Thus, the sludge should be removed and drained within a relatively short time frame.

A few exploratory experiments have been carried out to upgrade the sludge quality and to recover the oil. For example, by adjusting the pH of the sludge to about one with HCl, phase separation takes place. Separation by centrifuging was found to yield an oily sludge phase of about 60% oil. Additional work is necessary in this area to determine the best technique for oil recovery.

AN APPROACH TO AUTOMATIC CONTROL

To develop any type of automated system, it first is necessary to establish the parameters to be monitored and controlled. For the electrolytic oily wastewater treatment process, the response to be measured is the effluent oil concentration. Even though the treatment effectiveness is not always predictable based strictly on influent oil content, the degree of treatment, or effluent water quality, as shown in this study is dependent on the ratio of the amount of iron dissolved to the amount of oil in the influent. Thus, the effluent oil content will be determined by the iron dissolution rate which in turn is determined by the electrode current. Consequently, the effluent oil concentration may be controlled by using it as a response to control the current. Other parameters such as flow rate and salt concentration would be kept constant.

The effluent oil concentration that can be discharged from the electrolytic cell is governed by imposed environmental regulations. The standard method employed to determine oil concentration directly is based upon a solvent extraction technique (7) which is time consuming and for that reason cannot be used for feedback control.

Analytical instruments to measure directly the oil concentration are available, such as infrared and ultraviolet spectrophotometers. These instruments were not evaluated in depth in the present program; however, they are expensive and may require skilled operators.

As was shown in this study, light scattering or turbidity of the wastewater correlates with effluent oil content with a correlation coefficient of 0.88. Since turbidity is a simple measurement with a rapid response, it may be used to monitor effluent water quality and the signal used to set the current. By using feedback control, the required water quality with minimum iron addition and minimum sludge generation can be obtained from the process.

With an arbitrary initial current setting, it is envisioned that a water sample would be acquired downstream of the cathode, sandfiltered to remove iron/oil floc, and its turbidity measured. The millivolt response from the instrument would be programmed into a microprocessor and compared to a preset value which corresponds to the desired water quality. A current change would then be made, either increased or decreased depending on whether turbidity is above or below the set point. The magnitude of the current change would be related to the magnitude of the difference between the signal and the set point. The time interval between resetting and the next sampling will depend upon the flow time between the electrode and the sampling point. The system would continue to search for minimum current by examining changes in turbidity. The upper bound on the current would be the passivation current (current density of 10 mA/cm^2).

To avoid large and rapid excursions in influent oil concentration, an equalization tank, capable of containing a few hours of the plant flow should be employed. This would allow designing the electrode size for a time averaged oil content (rather than peak) and reduce the requirement for rapidity of response of the control system.

Maintenance requirements, such as the means to assure clear instrument windows, remain to be established.

SYSTEM CAPACITY DESIGN CRITERIA

To design a treatment cell, the main feature that needs to be established is the size of the electrode. This will determine, at the passivation current density, the amount of iron which can be dissolved to produce a desired effluent quality. The required total current is proportional to the influent oil flux, which is in turn proportional to the flow rate and oil concentration (1). For the Livonia Plant wastewater, examination of the data, along with previous experience (1), indicates that in most instances, a current of 0.007 amperes per liter per minute of flow per (ppm) of influent oil concentration is adequate to provide an effluent with less than 25 ppm of Freon extractables. Since current density is limited by passivation to about 100 A/m^2, the electrode area required can be estimated at about 7×10^{-5} square meters per liter per minute per (ppm). For example, to treat 38 l/min (10 gal/min) of wastewater containing 2000 ppm of oil would require 5.3 m^2 of electrode area.

In designing a system for a particular plant site, it is recommended that simple beaker or small bench scale studies be carried out to establish the electrode area design constant for that wastewater to obtain the desired water quality.

ECONOMIC PROJECTIONS

To establish the overall economics of the electrolytic process accurately is difficult at this time. It will be necessary to have a scaled-up process handling a major portion of a manufacturing plant effluent to determine electrode durability, maintenance, manpower requirements, etc. These have not been fully addressed in this study. Nevertheless, some preliminary economic estimates of operating and capital costs can be made from the current studies. Economics projections for a few scenarios are presented below.

Scheme 1. A process scheme with air bubblers and without automation.

This situation represents the approach used during the first phase of the program. The system would represent the least expensive approach both from a capital investment and direct operating cost standpoint. However, as previously noted, there may be a deficiency of effectiveness of the air bubblers after some time of operation. This would lead to rapid loading of the sand filter.

Assuming a plant size of about 76 m^3/day (20,000 gal/day) the capital requirements would be about $50,000 including flow meters, pumps, power supplies, etc. The capital costs are itemized in Table 12. Direct operating costs based on the present study include $0.04/$m^3$ ($0.15/1000 gal) electrical (at $0.025/kW-hr), $0.04/$m^3$ ($0.15/1000 gal) calcium chloride (at $0.07/kg), and $0.01/$m^3$ ($0.04/1000 gal) for iron based on iron scrap value. This equals $0.09/$m^3$ ($0.34/1000 gal) of wastewater treated. This cost would be the same for all of the schemes described in this section since the major costs are electrical, salt, and iron. Added to this would be the operating costs associated with flotation air, pumps, motors, etc. For comparison, direct chemical costs for common batch systems generally range from around $0.22-$0.29/m^3 ($0.85 to $1.10/1000 gals). Credit for the waste oil is not included.

Scheme 2. A process scheme with dissolved air flotation and without automation.

The major advantages of this scheme are that flotation and skimming would be much more efficient and would occupy much less space than Scheme 1. Both capital and operating costs would be increased. Capital would be increased by $30,000 for a dissolved air unit capable of handling from 19 to 114 m^3/day (5,000 to 30,000 gal/day). Operating costs for this unit, based on information furnished by the manufacturer, average about $0.08/$m^3$ ($0.30/1000 gal). This includes cost of pumping, skimming, etc. With automatic skimming, manpower costs would decrease and the quality of the sludge may be improved. Other costs would be similar to Scheme 1 with only minor saving of manpower.

Scheme 3. A process with dissolved air flotation and automated control.

This scheme would be the most efficient from a manpower standpoint and would result in optimum operation. The automatic feedback control technique remains to be evaluated. The feedback system envisioned would control the current by sensing the oil content in the effluent from the cell. Systems to monitor the oil range from $800 to $8,000 depending on the plant wastewater to be treated. For Livonia Plant wastewater, a system to monitor turbidity, which was shown to correlate with oil content, may be employed. In this case, a total feedback system would be around $5,000 with no increase in direct operating cost. Manpower would be decreased since adjustment and settings of the process would be automated. Maintenance cost of the feedback system is not known.

TABLE 12. CAPITAL COSTS OF ELECTROLYTIC TREATMENT

1. Process with air bubblers-without automation

Flow equalization tank	-	$10,000
Pumps	-	2,500
Mixing tank	-	1,500
Electrolytic cell-shell	-	3,000
Power supplies	-	8,000
Belt skimmer	-	3,500
Sludge collector	-	3,000
Flow meters	-	1,500
Electrode	-	2,500
Air bubblers	-	2,000
Air compressor	-	2,000
Sand filter	-	1,500
Installation	-	9,000
		$50,000

2. Process with dissolved air flotation-without automation

Scheme 1 costs	-	$50,000
Dissolved air flotation	-	30,000
		$80,000

3. Process with dissolved air flotation-with automation

Scheme 2 costs	-	$80,000
Automation (turbidity system)	-	5,000
		$85,000

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